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Ground state of an optical bipolaron with an intermediate strength of coupling

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Abstract

The ground-singlet state of an optical bipolaron in the region of intermediate coupling strengths is analysed. It is shown that the spatial structure of a bipolaron with intermediate coupling strength is that of an axially symmetric quasi-molecular dimer. The bipolaron energies of coupling are determined for different coupling constants and dielectric parameters of a medium. The electronic terms of the ground-dimer state are represented as a function of the distance between quasi-particles. The intermediate region of coupling constants is shown to give rise to an additional specific term in the total energy, which depends on the dielectric properties of a medium and makes the bipolaron energy of coupling higher (at $\varepsilon^*/\varepsilon_\infty > 1.06$) or lower (at $\varepsilon^*/\varepsilon_\infty < 1.06$) than the value in the limit of adiabatic and strong coupling.

1. Introduction

The problem of the existence of bipolarons in polar media has been repeatedly analysed theoretically [1–11]. These works are mainly concerned with the ground-electronic state of a bipolaron in the limit of a strong electron–phonon coupling (with dimensionless coupling constant $\alpha_c > 10$). They contain contradictory data on both the possibility of the existence of bipolarons in principle and the magnitude of their coupling energy. However, in actual practice, most media are characterized by the so-called intermediate coupling strength ($\alpha_c \sim 5$–10). Formally, the approaches of the method of strong coupling are inapplicable in this case and one should use methods of intermediate coupling strength.

In the present work, we study the ground-electronic state of a singlet-optical bipolaron in the region of intermediate coupling constants and compare our quantitative results with the previously known data [2, 3] for the limiting case of adiabatic and strong electron–phonon coupling.

The analysis is based on the method of arbitrary coupling strength, developed by Buimistrov and Pekar [12]. The accuracy of the method compares well with that of the method of functional integration [13] and makes it possible to obtain the total energy of an optical polaron in the intermediate region of coupling constants, whose position on the energy

scale is lower by approximately 5% than the value obtained by the Feynman method [13]. The special feature of the method [12] is that it takes into account the dependence of the equilibrium positions of quantum field oscillators in the presence of charged particles on the coordinates of the particles themselves. This means that ions respond not only to the average electron field, but to the instantaneous electron field as well. With increasing coupling strength, the dependence on the coordinates becomes weaker and the results produced by the method are approaching in a natural way those for the case of strong coupling.

2. Method and basic equations

For a non-degenerate electron band, the Hamiltonian of a two-electron system interacting with longitudinal optical phonons of the dielectric continuum can be written in the isotropic effective mass approximation in the form

$$H = \sum_{j=1,2} \frac{p_j^2}{2m^*} + \sum_{\vec{f},j=1,2} A_j \left[\exp\left(\mathrm{i}\vec{f}\vec{r}_j\right) b_{\vec{f}} + \exp\left(-\mathrm{i}\vec{f}\vec{r}_j\right) b_{\vec{f}}^+ \right] + \frac{1}{2} \sum_{\vec{f}} \hbar\omega_{\vec{f}} \left(b_{\vec{f}} b_{\vec{f}}^+ + b_{\vec{f}}^+ b_{\vec{f}} \right) + \frac{e^2}{\varepsilon_\infty |\vec{r}_1 - \vec{r}_2|}. \tag{1}$$

The Hamiltonian (1) is valid in the case when the energy surface has a spherical shape and the minimum of the surface in the $\vec{K}$ space coincides with the point $\vec{K} = 0$. In the Hamiltonian (1), the following notation is used: $b_{\vec{f}}$ and $b_{\vec{f}}^+$ are the Bose creation and annihilation operators for a longitudinal optical phonon with wave vector $\vec{f}$ and frequency $\omega_{\vec{f}}$; $\vec{r}_j$ is the radius vector of j-th electron, with the origin of coordinates coinciding with the polaron's centre of gravity; m^* is the effective electron mass at the conduction band bottom. The last term in (1) describes the screened direct Coulomb interaction between electrons. In the present work, we use complex coordinates of running plane waves in contrast to the method [12] employing standing waves normalized to the volume V for the Hamiltonian of lattice vibrations.

The Fourier coefficients A_f characterizing the interaction of an electron with longitudinal optical phonons has the form

$$A_f = 2\alpha_\mathrm{c} \frac{\hbar\omega_f}{\left|\vec{f}\right|} \left(\frac{\pi\hbar^2\varepsilon^*}{Ve^2m^*} \right)^{1/2} \qquad \alpha_\mathrm{c} = \frac{e^2}{2\varepsilon^*\hbar\omega_f} \left(\frac{2m^*\omega_f}{\hbar} \right)^{1/2}. \tag{2}$$

Here, V is the volume of the main region of periodicity, $1/\varepsilon^* = \varepsilon_\infty^{-1} - \varepsilon_\mathrm{s}^{-1}$ is the effective dielectric constant of the medium, and α_c is the dimensionless electron–phonon coupling constant.

In what follows it is convenient to pass in the Hamiltonian (1) from the operators b_f and b'_f to normal coordinates and the canonically conjugate phonon momenta

$$q_f = \frac{b_f + b_{-f}^+}{\sqrt{2}} \qquad q_f^* = q_{-f} \qquad p_f = -\mathrm{i}\,\frac{b_f - b_{-f}^+}{\sqrt{2}} \qquad p_f^* = p_{-f} \tag{3}$$

with the conventional quantization conditions for the dimensionless operators: $[q_f, p_{f_1}] = \mathrm{i}\delta_{ff_1}$, $[q_f, q_{f_1}] = [p_f, p_{f_1}] = 0$. Using transformation (3), the Hamiltonian (1) can be written in the form

$$H = \sum_{j=1,2} \frac{p_j^2}{2m^*} + \sum_{\vec{f},j=1,2} A_f \left[\exp\left(\mathrm{i}\vec{f}\vec{r}_j\right) q_{\vec{f}} + \exp\left(-\mathrm{i}\vec{f}\vec{r}_j\right) q_{-\vec{f}} \right]$$

$$+\frac{1}{2}\sum_{\vec{f}}\hbar\omega_{\vec{f}}\left(q_{\vec{f}}q_{-\vec{f}}+p_{\vec{f}}p_{-\vec{f}}\right)+\frac{e^2}{\varepsilon_\infty|\vec{r}_1-\vec{r}_2|}. \tag{4}$$

Let us make a change from the coordinates $q_{\vec{f}}$ to the new coordinates $q'_f=q_f-q^0_f(\vec{r}_1,\vec{r}_2)$. Here, $q^0_f(\vec{r}_1,\vec{r}_2)$ are the equilibrium positions of the quantum field oscillators, dependent on the coordinates $\vec{r}_j$. When written in terms of new variables, the Hamiltonian (4) has the form

$$\begin{aligned}H=&-\sum_{j=1,2}\frac{\hbar^2}{2m^*}\Bigg[\Delta_j-2\sum_{\vec{f}}\left[\nabla_j q^0_f\left(\vec{r}_j\right),\nabla_j\right]\frac{\partial}{\partial q'_f}-\sum_{\vec{f}}\left[\nabla_j q^0_f(\vec{r}_j)\right]\frac{\partial}{\partial q'_f}\\&+\sum_{\vec{f},\vec{f}_1}\left[\nabla_j q^0_f\left(\vec{r}_j\right),\nabla_j q^0_{f_1}\left(\vec{r}_j\right)\right]\frac{\partial^2}{\partial q'_f\partial q'_{f_1}}\Bigg]+\frac{e^2}{\varepsilon_\infty|\vec{r}_1-\vec{r}_2|}\\&+\sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\left[\left[q^0_f\left(\vec{r}_j\right)+q'_f\right]\left[q^0_{-f}\left(\vec{r}_j\right)+q'_{-f}\right]-\frac{\partial^2}{\partial q'_f\partial q'_{-f}}\right]\\&+\sum_{\vec{f},j=1,2}A_f\left\{\exp\left(\mathrm{i}\vec{f}\vec{r}_j\right)\left[q^0_{\vec{f}}\left(\vec{r}_j\right)+q'_f\right]+\exp\left(-\mathrm{i}\vec{f}\vec{r}_j\right)\left[q^0_{-f}(\vec{r}_j)+q'_{-f}\right]\right\}.\end{aligned} \tag{5}$$

Following the method [12], we approximate the total wave function of the electron–phonon system by the multiplicative form $\Psi=\varphi(\vec{r}_1,\vec{r}_2)\Phi(\ldots q'_f\ldots)$, where $\varphi(\vec{r}_1,\vec{r}_2)$ is the symmetrized two-centre two-electron wave function (in the general case under consideration, the centres of gravity of two polarons are not spatially coincident and the distance between them is R [2]) and $\Phi(\ldots q'_f\ldots)$ is the wave function describing the motion of displaced quantum field oscillators. As shown in [8,11], the multiplicative approximation to the function is suitable for all values of the coupling constant α_c.

Using the multiplicative approximation to the wave function and taking into account that each of the functions $\varphi(\vec{r}_1,\vec{r}_2)$ and $\Phi(\ldots q'_f\ldots)$ is normalized individually, we obtain from (5) the following functional of the total energy of the system

$$\begin{aligned}Q[\Psi]=&-\sum_{j=1,2}\frac{\hbar^2}{2m^*}\int\left|\nabla_j\varphi(\vec{r}_1,\vec{r}_2)\right|^2\mathrm{d}\tau_j+\sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\left\langle\varphi\left|q^0_f\left(\vec{r}_j\right)q^0_{-f}\left(\vec{r}_j\right)\right|\varphi\right\rangle+\left\langle\varphi\left|\frac{e^2}{\varepsilon_\infty r_{12}}\right|\varphi\right\rangle\\&+\sum_{\vec{f},j=1,2}A_f\left[\left\langle\varphi\left|\exp\left(\mathrm{i}\vec{f}\vec{r}_j\right)q^0_f\left(\vec{r}_j\right)+\exp\left(-\mathrm{i}\vec{f}\vec{r}_j\right)q^0_{-f}\left(\vec{r}_j\right)\right|\varphi\right\rangle\right]\\&-\sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\alpha_f(j)\left\langle\Phi\left|\frac{\partial^2}{\partial q'_f\partial q'_{-f}}\right|\Phi\right\rangle+\sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\left\langle\Phi\left|q'_fq'_{-f}\right|\Phi\right\rangle\\&+\sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\left[\beta_f(j)\left\langle\Phi\left|q'_f\right|\Phi\right\rangle+\beta_{-f}(j)\left\langle\Phi\left|q'_{-f}\right|\Phi\right\rangle\right].\end{aligned} \tag{6}$$

Here, $\vec{r}_{12}=\vec{r}_1-\vec{r}_2$ and

$$\begin{aligned}\alpha_f(j)&=1+\frac{\hbar}{m^*\omega_f}\left\langle\varphi\left|\frac{\partial q^0_{f_1}}{\partial\vec{r}_j}\frac{\partial q^0_f}{\partial\vec{r}_j}\right|\varphi\right\rangle\\\beta_f(j)&=\left\langle\varphi\left|q^0_{-f}\left(\vec{r}_j\right)\right|\varphi\right\rangle+\frac{2A_f}{\hbar\omega_f}\left\langle\left|\exp\left(\mathrm{i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle.\end{aligned} \tag{7}$$

When deriving (6), we took into account that $\langle\Phi|\partial/\partial q_f|\Phi\rangle=0$.

Extremalizing the functional (6) for Φ, we can easily obtain a wave equation describing the oscillations of the quantum polarization field in the presence of charges,

$$-\alpha_f(j)\frac{\partial^2}{\partial q'_f \partial q'_{-f}}\Phi + \left[q'_f q'_{-f} + \beta_f(j) q'_f + \beta_{-f}(j) q'_{-f}\right]\Phi = \frac{2\lambda_f(j)}{\hbar\omega_f}\Phi\,. \quad (8)$$

From equation (8) we have

$$\lambda_f(j) = \frac{\hbar\omega_f}{2}\left[\left(1+2n_f\right)\sqrt{\alpha_f(j)} - \beta_f^2(j)\right] \quad n_f = 0, 1, 2, \ldots. \quad (9)$$

Excluding from the functional (6) the coordinates q'_f and using (8) and (9), we obtain the bipolaron (bp) functional

$$\begin{aligned} Q_{\rm bp}[\varphi] =& -\sum_{j=1,2}\frac{\hbar^2}{2m^*}\int\left|\nabla_j\varphi\left(\vec{r}_1,\vec{r}_2\right)\right|^2 {\rm d}\tau_j - \sum_{\vec{f},j=1,2}\frac{2A_f^2}{\hbar\omega_f}\left\langle\varphi\middle|\exp\left(-{\rm i}\vec{f}\vec{r}_j\right)\middle|\varphi\right\rangle\left\langle\varphi\middle|\exp\left({\rm i}\vec{f}\vec{r}_j\right)\middle|\varphi\right\rangle \\ &+ \sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\left[\left\langle\varphi\left|q_f^0(j)q_{-f}^0(j)\right|\varphi\right\rangle - \left\langle\varphi\left|q_f^0(j)\right|\varphi\right\rangle\left\langle\varphi\left|q_{-f}^0(j)\right|\varphi\right\rangle\right] + \left\langle\varphi\left|\frac{e^2}{\varepsilon_\infty r_{12}}\right|\varphi\right\rangle \\ &+ \sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\left(1+2n_f\right)\left(1+\frac{\hbar}{2m^*\omega_f}\left\langle\varphi\left|\frac{\partial q_{-f}^0\partial q_f^0}{\partial\vec{r}_j\partial\vec{r}_j}\right|\varphi\right\rangle\right) \\ &+ \sum_{\vec{f},j=1,2}A_f\left[\left\langle\varphi\left|\exp\left({\rm i}\vec{f}\vec{r}_j\right)q_f^0(\vec{r}_j)\right|\varphi\right\rangle - \left\langle\varphi\left|\exp\left({\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\left|q_{-f}^0\left(\vec{r}_j\right)\right|\varphi\right\rangle\right] \\ &+ \sum_{\vec{f},j=1,2}A_f\left[\left\langle\varphi\left|\exp\left(-{\rm i}\vec{f}\vec{r}_j\right)q_{-f}^0\left(\vec{r}_j\right)\right|\varphi\right\rangle - \left\langle\varphi\left|\exp\left(-{\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\left|q_f^0\left(\vec{r}_j\right)\right|\varphi\right\rangle\right]. \quad (10) \end{aligned}$$

The vibrational quantum numbers take the values $n_f = 0, 1, 2, \ldots$. To determine the displacements q_f^0 and q_{-f}^0, we have to extremalize the functional (8) and find the equations describing the change in q_f^0 and q_{-f}^0. However, it is more convenient to use the approximation from [12], which gives for the one-particle state correct results in the limits of weak and strong coupling

$$q_f^0(\vec{r}_1,\vec{r}_2) = \sum_{j=1,2}c_f(j)\exp\left({\rm i}\vec{f}\vec{r}_j\right) \quad (11)$$

where $c_f(j)$ is variational parameter determined by minimizing the functional

$$\begin{aligned} Q_{\rm bp}[\varphi] =& -\sum_{j=1,2}\frac{\hbar^2}{2m^*}\int\left|\nabla_j\varphi\left(\vec{r}_1,\vec{r}_2\right)\right|^2 {\rm d}\tau_j - \sum_{\vec{f},j=1,2}\frac{2A_f^2}{\hbar\omega_f}\left\langle\varphi\middle|\exp\left(-{\rm i}\vec{f}\vec{r}_j\right)\middle|\varphi\right\rangle\left\langle\varphi\middle|\exp\left({\rm i}\vec{f}\vec{r}_j\right)\middle|\varphi\right\rangle \\ &+ \sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}c_f(j)c_{-f}(j)\left[1-\left\langle\varphi\left|\exp\left(-{\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\varphi\left|\exp\left({\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\right] + \left\langle\varphi\left|\frac{e^2}{\varepsilon_\infty r_{12}}\right|\varphi\right\rangle \\ &+ \sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\left(1+2n_f\right)\left(1+\frac{\hbar}{2m^*\omega_f}c_f(j)c_{-f}(j)f^2\right) \\ &+ \sum_{\vec{f},j=1,2}\frac{\hbar\omega_f}{2}\left\{\left[c_f(j)+c_{-f}(j)\right]\left[1-\left\langle\varphi\left|\exp\left(-{\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\varphi\left|\exp\left({\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\right]\right\} \quad (12) \end{aligned}$$

with the variation parameter given by

$$c_{-f}(j) = -\frac{2A_f}{\hbar\omega_f}\frac{1-\left\langle\varphi\left|\exp\left({\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\varphi\left|\exp\left(-{\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle}{\hbar\left(2m^*\omega_f\right)^{-1}f^2\left(1+n_f\right)+1-\left\langle\varphi\left|\exp\left({\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\varphi\left|\exp\left(-{\rm i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle}\,. \quad (13)$$

Substituting the parameters (13) into the initial functional (12) and taking into account that $c_f(j) = c_{-f}(j)$, we obtain the following expression for the total energy of a bipolaron with an intermediate coupling strength

$$Q_{\rm bp}[\varphi] = -\sum_{j=1,2}\frac{\hbar^2}{2m^*}\int\left|\nabla_j\varphi\left(\vec{r}_1,\vec{r}_2\right)\right|^2\mathrm{d}\tau_j + \left\langle\varphi\left|\frac{e^2}{\varepsilon_\infty r_{12}}\right|\varphi\right\rangle$$
$$-\sum_{\vec{f},j=1,2}\frac{2A_f^2}{\hbar\omega_f}\left\langle\varphi\left|\exp\left(-\mathrm{i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\varphi\left|\exp\left(\mathrm{i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle + \sum_{\vec{f}}\frac{\hbar\omega_f}{2}\left(1+n_f\right)$$
$$-\sum_{\vec{f},j=1,2}\frac{A_f^2}{\hbar\omega_f}\frac{\left[1-\left\langle\varphi\left|\exp\left(\mathrm{i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\varphi\left|\exp\left(-\mathrm{i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\right]^2}{\hbar\left(2m^*\omega_f\right)^{-1}f^2\left(1+2n_f\right)+1-\left\langle\varphi\left|\exp\left(\mathrm{i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle\left\langle\varphi\left|\exp\left(-\mathrm{i}\vec{f}\vec{r}_j\right)\right|\varphi\right\rangle} \tag{14}$$

$$Q_{\rm bp}[\varphi] = J_{\rm bp}[\varphi] - G_{\rm bp}[\varphi] + \sum_{\vec{f}}\frac{\hbar\omega_f}{2}\left(1+n_f\right) = F_{\rm bp}[\varphi] + \sum_{\vec{f}}\frac{\hbar\omega_f}{2}\left(1+n_f\right). \tag{15}$$

The energy of a free electron with effective mass m^* at the bottom of the conduction band is taken as zero energy. The functional (14) depends only on the function φ. The integro-differential equation for the function can be found from the extremum condition for this functional.

The contribution of the component $G_{\rm bp}[\varphi]$ to the total functional is determined by the last term in (15) and is specific to the method of intermediate strength of coupling. In the limit of strong coupling it tends to a constant.

The functional $J_{\rm bp}[\varphi]$ includes three first terms from (14) and determines the total self-consistent energy of the two-polaron system in the limit of strong coupling, proportional to $\alpha_{\rm c}$. An analysis of the functional $F[\varphi]$ for the one-electron case has shown [12] that it describes reliably one-particle states in both the limiting cases, corresponding to strong and weak electron–phonon coupling. The limit of strong coupling gives a result corresponding to the adiabatic approximation, and that of weak coupling, a result corresponding to the second-order approximation of the perturbation theory.

For the two-particle problem, the self-consistent functional $J_{\rm bp}[\varphi]$ was discussed in detail in [2–5], with account taken of the dynamic interelectron correlations, as a function of the distance R between polarons and of the dielectric parameters of the medium. Making in the functional $J_{\rm bp}[\varphi]$ a change from the f representation to the coordinate representation, we can write it in the two-particle case in the form

$$J_{\rm bp}[\varphi] = \sum_{j=1,2}\frac{\hbar^2}{4m^*}\int\nabla_j^2\rho_1\left(\vec{r}_j\right)\mathrm{d}\tau_j - \frac{1}{4}\int\mathrm{d}\tau_1\mathrm{d}\tau_2\rho_2\left(\vec{r}_1,\vec{r}_2\right)$$
$$\times\left[\frac{1}{\varepsilon^*}\sum_{j=1,2}\rho_1\left(\vec{r}_j'\right)g\left(\vec{r}_j,\vec{r}_j'\right)\mathrm{d}\tau_j' - \frac{2}{\varepsilon_\infty}g\left(\vec{r}_1,\vec{r}_2\right)\right] \tag{16}$$

where $g(\vec{r}_1,\vec{r}_2) = e^2/r_{12}$ is the operator of the interelectron interaction and $\rho_1(\vec{r}_1)$ and $\rho_2(\vec{r}_1,\vec{r}_2)$ are the one- and two-particle functions of electron density [2–5]. The interpolaron distance R appears in (16) as a parameter. In the zero approximation, the symmetrized two-particle wave function $\varphi(\vec{r}_1,\vec{r}_2)$ is chosen in the Heitler–London form

$$\varphi\left(\vec{r}_1,\vec{r}_2\right) = N\left[\chi_{s,a}\left(\vec{r}_1\right)\chi_{s,b}\left(\vec{r}_2\right) + \chi_{s,b}\left(\vec{r}_1\right)\chi_{s,a}\left(\vec{r}_2\right)\right] \tag{17}$$

where the one-electron spherically symmetric wave functions $\chi_{s,a}(\vec{r}_1)$ and $\chi_{s,b}(\vec{r}_2)$ have the centres a and b, which coincide with the centres of gravity of the polarons, and are spatially

separated by a distance R; $N = (1+S^2)^{-1/2}$, and $S = \langle \chi_{s,a}(r)|\chi_{s,b}(r)\rangle$ is the overlap integral. Using the wave function (17), the functional (16) can be rewritten in the form

$$J_{\rm bp} = \frac{\hbar^2}{2m^*\left(1+S^2\right)} \int \left[\left|\nabla_1 \chi_{s,a}(r_1)\right|^2 + 2S\nabla_1\chi_{s,a}(r_1)\,\nabla_1\chi_{s,b}(r_1) + \left|\nabla_1\chi_{s,b}(r_1)\right|^2 \right] {\rm d}\tau_1 - \frac{e^2}{2\varepsilon^*\left(1+S^2\right)^2}\left(I_1 + 4S^2 I_2 + I_3 + 8SI_4 + 2I_5\right) + \frac{e^2}{2\varepsilon_\infty\left(1+S^2\right)}\left(I_1 + 2I_2 + I_3\right) \tag{18}$$

with the following designations used for two-centre integrals

$$I_1 = \int \chi^2_{s,a}(r_1)\,\chi^2_{s,b}(r_1)\,r_{12}^{-1}{\rm d}\tau_1{\rm d}\tau_2 \qquad I_2 = \int \chi_{s,a}(r_1)\,\chi_{s,b}(r_1)\,\chi_{s,a}(r_2)\,\chi_{s,b}(r_2)\,r_{12}^{-1}{\rm d}\tau_1{\rm d}\tau_2$$

$$I_3 = \int \chi^2_{s,b}(r_1)\,\chi^2_{s,a}(r_1)\,r_{12}^{-1}{\rm d}\tau_1{\rm d}\tau_2 \qquad I_4 = \int \chi_{s,a}(r_1)\,\chi_{s,b}(r_1)\,\chi^2_{s,a}(r_2)\,r_{12}^{-1}{\rm d}\tau_1{\rm d}\tau_2$$

$$I_5 = \int \chi^2_{s,a}(r_1)\,\chi^2_{s,a}(r_1)\,r_{12}^{-1}{\rm d}\tau_1{\rm d}\tau_2 \tag{19}$$

In subsequent refinements of the energy of the system, we added complexity to the electron part of the wave function by including the interelectron correlation effects. The method of inclusion of these correlations, described in [2–5], assumes that the spectrum of the one-electron problem is known. The importance of taking into account the interelectron correlations when finding the coupling energy in self-trapped two-electron systems was noted in [14]. In this case the coupling is determined by the screening of the direct Coulomb repulsion by the phonon exchange effects, and the interaction potential, by the pair forces depending on the interelectron distance r_{12}.

The one-particle spherically symmetric 1s wave functions for the ground-electronic state of an optical polaron were chosen in the form

$$\chi_s(r) = \left(\frac{\alpha^3}{7\pi}\right)^{1/2}(1+\alpha r)\exp(-\alpha r) \tag{20}$$

where α is the variational parameter determined from the minimum condition for the functional $F_{\rm bp}[\varphi]$; the origin of co-ordinates is coincident with the centre of gravity of a polaron at the centre a. The use of the wave function approximation in the form (20) in the direct variation method gives the total energy of the one-particle state, differing from the result obtained by direct numerical solution of the nonlinear integro-differential Euler equation [15] by a fraction of a percent.

In the general case, when making numerical calculations with the use of the two-electron functional $F_{\rm bp}[\varphi]$ on the basis of two-centre wave functions, one comes up against the problem of calculation of two-centre integrals (19). To overcome this problem, we use the method [16] which reduces the wave function centred at b to the centre a, thereby reducing the two-centre integrals to one-centre integrals. With this method employed, the radial part $R_s(r)$ of the wave function $\chi_{s,b}(r)$ in the coordinates related to the centre a can be expressed in the following way

$$R_s(r) = \frac{\pi}{\alpha^2 C r}\left[\left(A_1 - A_2 r + A_3 r^2\right)\exp(\alpha r) - \left(A_1 + A_2 r + A_3 r^2\right)\exp(-\alpha r)\right]\exp(-C) \quad r < R$$

$$R_s(r) = \frac{\pi}{\alpha^2 C r}\left[\left(B_1 - B_2 r + B_3 r^2\right)\exp(-\alpha r)\right] \qquad r > R \tag{21}$$

where

$$A_1 = 2\left(3 + 3C + C^2\right) \qquad A_2 = 2\alpha(3+2C) \qquad A_3 = 2\alpha^2$$

$$A_4 = 2\left(3 - 3C + C^2\right) \qquad A_5 = 2\alpha(3 - 2C) \qquad C = \alpha R$$
$$B_1 = A_4 \exp(C) - A_1 \exp(-C) \qquad B_2 = A_5 \exp(C) - A_2 \exp(-C)$$
$$B_3 = A_3[\exp(C) - \exp(-C)]\,.$$

In formula (21), the electron coordinate r is reckoned from the centre a. The calculation of the integrals appearing in (15) on the basis of functions (20) and (21) is no particular problem, and the result can be represented in terms of elementary functions, but the final expression for the total energy is too cumbersome and is not presented here for this reason. The reduction of the two-centre integrals to the one-centre integrals makes it possible to find the integrals in the functional (14) in the analytical form and obtain the result as a function of the wave vector $\vec{f}$ and distance R.

3. Results and discussion

Using the direct variational method, we calculated from the functional of total energy (15) the energy of coupling for a singlet bipolaron $\Delta F = F_{\rm bp} - 2F_{\rm p}$ as a function of the distance R between the centres of gravity of quasi-particles for fixed ratios of dielectric constants $\varepsilon^*/\varepsilon_\infty = 1.0$ (the limiting case of $\varepsilon_{\rm s} \gg \varepsilon_\infty$) (figure 1) and $\varepsilon^*/\varepsilon_\infty = 1.08$ (figure 2) for the coupling constants $\alpha_{\rm c} = 5$, 7 and 10. $F_{\rm p}$ is the total energy of a free optical polaron.

With decreasing distance between polarons, the polarization effects caused by each of them start to interfere, which lowers the total energy of the two-electron system and gives rise to a bound state. At $R \to 0$, the direct Coulomb interaction dominates over the polarization effects, which leads to the formation of a maximum of the binding-energy curve at the point $R = 0$. At $R \to \infty$, the two terms in braces in (16) give the conventional electrostatic interaction between classical charges, $e^2/\varepsilon_{\rm s}R$. In this case, a transition from the region of a minimum of the total bipolaron energy to the region of classical electrostatic repulsion naturally results in the formation of a potential barrier.

The case of $\varepsilon^*/\varepsilon_\infty = 1.0$ corresponds to the maximum possible bipolaron coupling energy for the given coupling constant. The region of permissible dielectric media characterized by

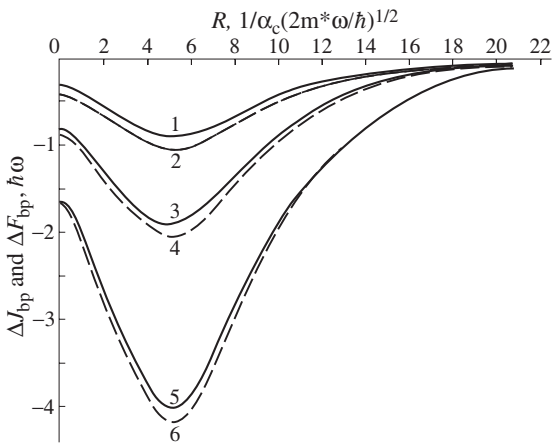

Figure 1. Bipolaron energy of coupling as a function of the distance between polarons for the coupling constants $\alpha_{\rm c} = 5$, 7 and 10 (curves 1, 3 and 5, respectively) and $\varepsilon^*/\varepsilon_\infty = 1.0$. The full curves are calculated by equation (15) (term $F_{\rm bp}$). The broken curves (2, 4 and 6, respectively) are plotted for $J_{\rm bp}$ corresponding to the limiting case of adiabatic and strong coupling.

the existence of stable bipolaron systems is defined by the inequality $\varepsilon^*/\varepsilon_\infty \leqslant 1.13$, being somewhat wider than that in the limit of the extremely strong coupling ($\varepsilon^*/\varepsilon_\infty \leqslant 1.125$ [2–5]) because of the inclusion of the additional term $G_{\rm bp}$. A quasi-stationary bipolaron system may exist in dielectric media with $\varepsilon^*/\varepsilon_\infty > 1.13$. In this case, the coupling energy $\Delta F_{\rm bp} > 0$, but, nevertheless, two-electron states are separated by a barrier from the state of uncoupled polarons. This value of the parameter $\varepsilon^*/\varepsilon_\infty$ is close to the previously found values of 1.13 [11] and 1.14 [7].

In concrete numerical calculations, we restricted our consideration to the case of a single branch of longitudinal polarization vibrations with the limiting frequency $\omega_f = \omega$, which corresponds to the long-wavelength limit $\vec{f} = 0$. Also, we chose for the lowest ground state the quantum number $n_f = 0$, i.e., the temperature (T) range was limited by the inequality $k_{\rm B}T \ll \hbar\omega$.

To compare the results for the intermediate coupling strength and strong coupling, we

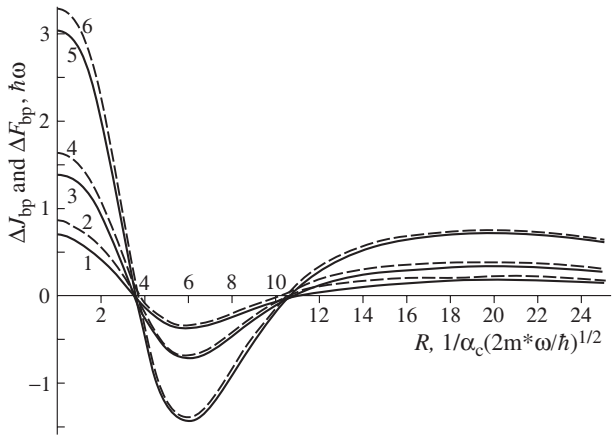

Figure 2. Bipolaron energy of coupling as a function of the distance between polarons for the coupling constants $\alpha_c = 5$, 7 and 10 (curves 1, 3 and 5, respectively) and $\varepsilon^*/\varepsilon_\infty = 1.08$. The full curves are calculated by equation (15) (term $F_{\rm bp}$). The broken curves (2, 4 and 6, respectively) are plotted for $J_{\rm bp}$ corresponding to the limiting case of adiabatic and strong coupling.

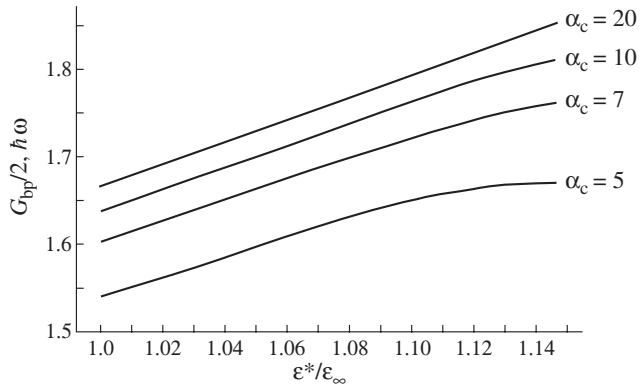

Figure 3. Variation of the additional term $G_{\rm bp}$ at the point of the minimum total energy with the ratio $\varepsilon^*/\varepsilon_\infty$ for different coupling constants α_c.

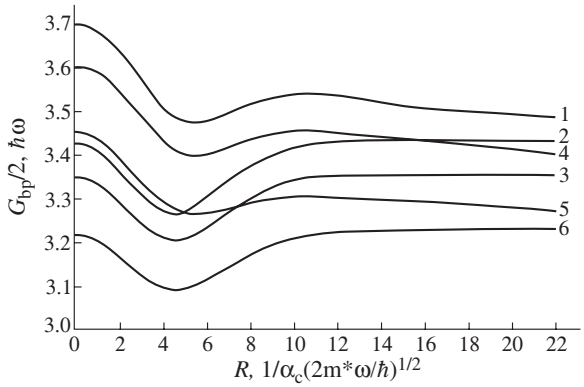

Figure 4. Variation of the additional term G_{bp} in the functional of total energy (15) with the distance between polarons for $\varepsilon^*/\varepsilon_\infty = 1.0$ (curves 1, 2 and 3) and 1.08 (curves 4, 5, and 6); $\alpha_c = 5$, (curves 1, 4), 7 (curves 2, 5) and 10 (curves 3, 6).

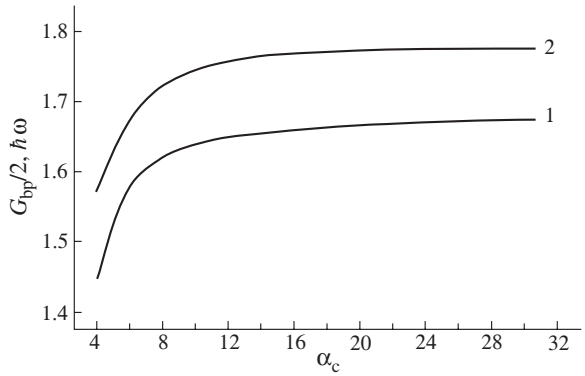

Figure 5. Variation of the additional term G_{bp} at the point of minimum total energy with the dimensionless coupling constant. Curve 1 corresponds to $\varepsilon^*/\varepsilon_\infty = 1.0$, and curve 2, to $\varepsilon^*/\varepsilon_\infty = 1.08$.

present in figures 1 and 2 the coupling energies $\Delta F_{bp} > 0$ and $\Delta J_{bp} = J_{bp} - 2J_p$ (here, $J_p = -0.1072\alpha_c^2\hbar\omega$). It can be readily seen from the figures that the inclusion of the additional term $G_{bp}[\varphi]$ into the total functional gives at intermediate coupling strengths a correction to the main functional $J_{bp}[\varphi]$ obtained in the adiabatic approximation. In the region of the interaction potential minimum, the contribution of the term ΔG_{bp} to the total coupling energy depends on both the ratio $\varepsilon^*/\varepsilon_\infty$ and the coupling constant. The effect of the inclusion of the additional term G_{bp} in the total energy on the bipolaron energy of coupling may vary. At $\varepsilon^*/\varepsilon_\infty = 1.0$, this contribution makes the coupling energy lower, with the contribution to the coupling energy being about 16% for $\alpha_c = 5$ and as low as 4% for $\alpha_c = 10$. At $\varepsilon^*/\varepsilon_\infty = 1.08$, the contribution of ΔG_{bp} is 5% and 1.7%, respectively, and the coupling energy increases. The change $\Delta G_{bp}/2$ at the point of minimum polaron interaction in a wide region of dielectric parameters is shown in figure 3. Near the critical value $\varepsilon^*/\varepsilon_\infty = 1.06$–$1.065$, the difference $G_{bp} - 2G_p$ reverses its sign. Here account is taken of the following polaron energies: $G_p = 1.622$, 1.688, 1.737 and $1.757\hbar\omega$, for coupling constants $\alpha_c = 5$, 7, 10 and 20, respectively. Thus, the contribution of G_{bp} makes the bipolaron coupling energy lower for $\varepsilon^*/\varepsilon_\infty < 1.06$ and higher for $\varepsilon^*/\varepsilon_\infty > 1.0$.

The variation of the additional term of the total energy, G_{bp}, with distance (figure 4) qualitatively reproduces the variation of the coupling energy associated with the contribution of J_{bp}, but the quantitative distinctions are significant. This behaviour of G_{bp} as a function of distance R makes it possible to minimize the functional J_{bp}, rather than the functional F_{bp}, in the variational calculations. The extreme values of the variational parameters obtained in this case can be further used to calculate the function F_{bp}. G_{bp} at the point of the minimum polaron interaction potential is shown as a function of the coupling constant in figure 5 for different $\varepsilon^*/\varepsilon_\infty$ values. The contribution of G_{bp} grows smoothly with increasing coupling constant, showing a tendency to saturate.

From figures 1 and 2 it can be seen that the bipolaron potential well becomes shallower with decreasing α_c. The critical values $\alpha_c^{(cr)}$ below which the connected bipolaron does not exist have been obtained previously: ~ 6.8 [17], 7.3 [7] and 9.3 [11]. Genarally, $\alpha_c^{(cr)}$ are functions of the parameter $\varepsilon^*/\varepsilon_\infty$: the higher $\varepsilon^*/\varepsilon_\infty$ the greater $\alpha_c^{(cr)}$. The following values of the critical parameters were obtained: $\alpha_c^{(cr)} \geqslant 5.3$ at $\varepsilon^*/\varepsilon_\infty = 1.00$, $\alpha_c^{(cr)} \geqslant 7.0$ at $\varepsilon^*/\varepsilon_\infty = 1.08$ and $\alpha_c^{(cr)} \geqslant 10$ at $\varepsilon^*/\varepsilon_\infty = 1.12$. The presence of a potential well does not mean yet the existence of a connected bipolaron. From figure 2 it follows that at $\varepsilon^*/\varepsilon_\infty = 1.08$ and $\alpha_c^{(cr)} = 5.0$ there is a bipolaron potential well. However, it can be shown using the method proposed in [18] that at $\alpha_c = 5$ no connected bipolaron is formed. The connected condition only appears at $\alpha_c^{(cr)} > 7.0$.

An analysis made for the ground-singlet term of an optical bipolaron showed that the bipolaron coupling energy at intermediate electron–phonon coupling constants is mainly determined by the term J_{bp} obtained in the limit of strong coupling, and the specific term G_{bp} introduces a correction. However, the region of permissible dielectric media ($\varepsilon^*/\varepsilon_\infty = 1.125$), determined in [2–5] and characterized by the possibility of existence of bipolaron systems becomes somewhat wider owing to the inclusion of this specific interaction.

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